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ISOLATION OF A NONANAPHTHENE FROM AN OKLAHOMA PETROLEUM [1]

By Joseph D. White [2] and Frank W. Rose, Jr.[2]

ABSTRACT

A nonanaphthene boiling at 136.65° C has been isolated from an Oklahoma petroleum. This has been accomplished by fractional crystallization, from a solution first in liquid propane and methane, and then in dichlorodifluoromethane, of the distillate boiling normally between 136 and 137° C after first removing the aromatic hydrocarbons present. Its boiling point, freezing point, density, refractive index, heat of fusion, and critical solution temperature in aniline have been determined.

Its empirical formula of C_9H_{18} has been established, but its structural formula is not known. It is probably a derivative of cyclopentane. There is a remote possibility that it is a mixture of stereoisomers. It constitutes not more than 0.1 percent of the crude petroleum.

CONTENTS

I. INTRODUCTION

The term "naphthenes" was used by Markownikoff and Ogloblin [3] to designate those compounds occurring in petroleum which belong to the class of saturated monocyclic hydrocarbons having the empirical formula C_nH_{2n}. Those found in the lighter distillates of petroleum are chiefly the alkyl derivatives of cyclopentane and cyclohexane.

A "nonanaphthene" is a naphthene containing 9 carbon atoms. The one herein described is probably a derivative of cyclopentane, as will be pointed out later. It was found in the fraction of an Oklahoma petroleum which distilled normally between 135 and 137° C and was separated from other constituents by physical means.

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project No. 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] Research Associate at the National Bureau of Standards representing the American Petroleum Institute.

[3] Ber. Deut. Chem. Ges. 16(B), 1873 (1883).

II. PROCEDURE AND RESULTS

1. PRELIMINARY FRACTIONATION

The petroleum used in this work[4] was first systematically distilled, under the direction of S. T. Schicktanz, through the fractionating columns developed at this Bureau.[5] The distillation procedure varied for successive stages in the rectification. The final distillation was made in resistant glass stills having 30-plate columns, using a reflux ratio of 10:1 and a rate of about 1 ml/min—the distillate being separated into fractions for each degree rise in its boiling point. Figure

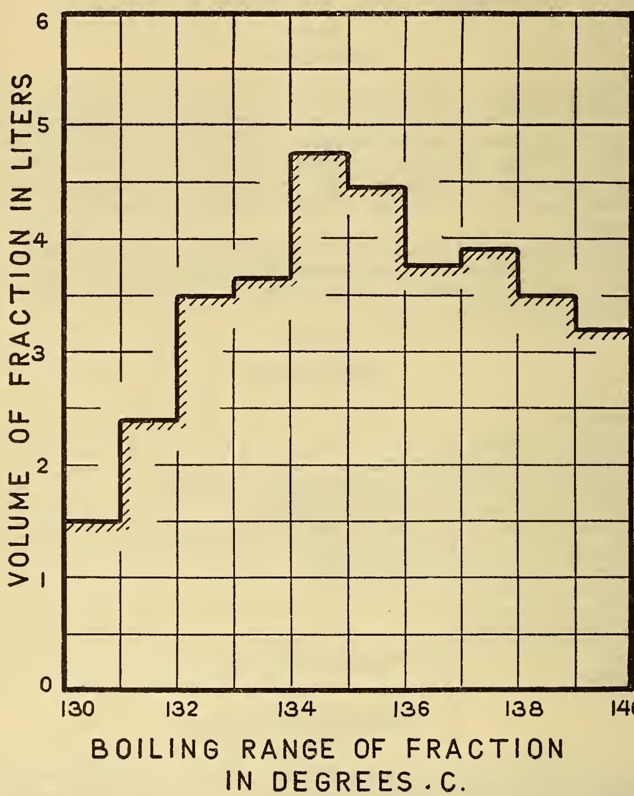

Figure 1.—*Volume distribution of petroleum fractions boiling between 130 and 140° C before removing any constituents.*

1 shows graphically the distribution by volume with respect to boiling range of the 35 liters distilling between 130 and 140° C. A large fraction which concentrated between 134 and 136° C is represented by a volume peak on the distillation graph.

All of the petroleum which boiled between 130 and 145° C was extracted with liquid sulphur dioxide to remove most of the aromatic hydrocarbons.[6] The residue was then distilled and extracted again. Following the second extraction, the immiscible portion was finally

[4] A description of the oil is given in BS J. Research 2, 469, table 1 (1929) RP45.
[5] BS J. Research 2, 470 (1929) RP45; 6, 378 (1931) RP282; 7, 851 (1931) RP379.
[6] BS J. Research 9, 714 (1932) RP501.

distilled, once at atmospheric pressure and 3 times at a pressure of 215 mm Hg, using the 30-plate columns as before but separating the distillate into 0.5° C cuts. In graph I of figure 2 the volume of each of these cuts is plotted against the boiling range. The boiling points indicated are those for a pressure of 215 mm Hg, the range 88 to 98° C corresponding approximately to the range 130 to 140° C at

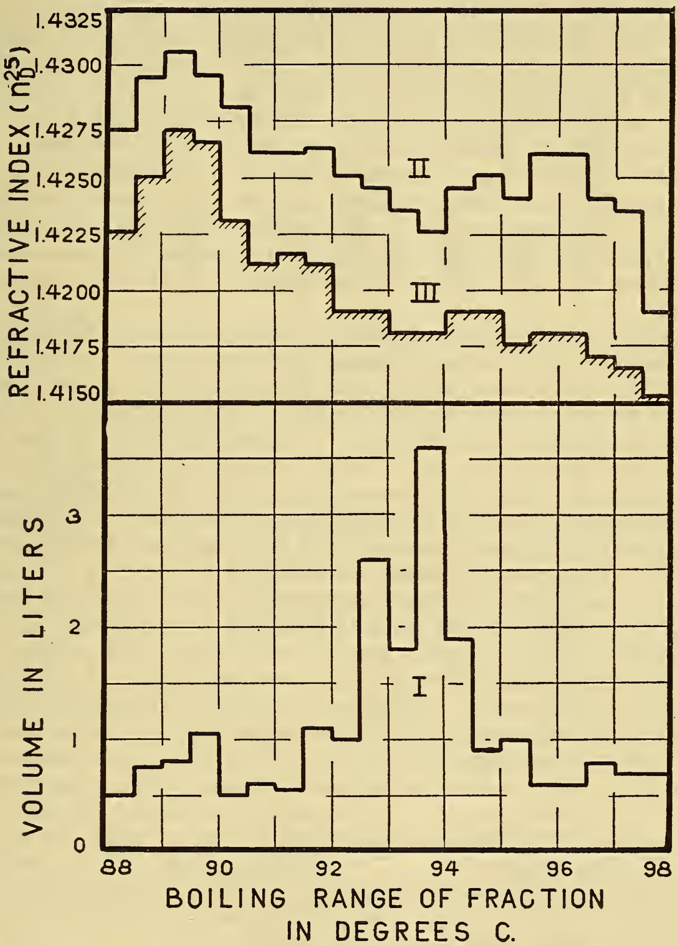

FIGURE 2.—*Volume distribution and refractive indices, with respect to boiling range at 215* mm, *of the petroleum fractions after extraction with sulphur dioxide and redistillation.*

Graph I, volume distribution; graph II, refractive indices; graph III, refractive indices after subsequent treatment with concentrated sulphuric acid.

760 mm Hg. The total volume of oil boiling in this region, after removing the aromatic constituents, was about 20 liters.

The largest single cut from the distillation was the 3.6 liters boiling between 93.5 and 94° C. Apparently a compound, or a constant-boiling mixture, had concentrated here. Its refractive index of 1.4227 [7] marked a minimum on the refractive index curve shown in

[7] The refractive indices throughout this paper are given for the D-line of sodium, and for a temperature of 25° C.

graph II of figure 2. This index was intermediate in value between those for the isononanes and nonanaphthenes known to boil near this temperature, a fact suggesting that the distillation fraction was a constant-boiling mixture composed of such hydrocarbons.

2. PRELIMINARY STUDY OF THE DISTILLATION FRACTIONS

The first step in the preliminary study of the constant-boiling mixture was to ascertain whether the xylene originally present had been completely extracted by the sulphur dioxide. Accordingly, a sample of the fraction was treated with an equal volume of nitrating mixture containing equal parts by volume of 3-percent fuming sulphuric acid and of fuming nitric acid, sp gr=1.50. A small amount of solid nitro-product was formed which was recrystallized from alcohol and treated further with nitrating mixture on a steam bath to yield the 2, 4, 6-trinitro-*m*-xylene. The refractive index of the residual oil was 1.4172 as compared with 1.4227 for the sample before nitration. This change in index indicated the presence of about 7 mole percent of xylene.

Nitration tests on other fractions boiling near 94° C showed that they also contained some aromatic hydrocarbons. It was therefore apparent that the aromatic constituents should be more completely removed before proceeding further with the identification or analysis of what remained. Accordingly, a 2-liter portion of the fraction boiling between 93.5 and 94° C and having $n_{25}=1.4226$ was stirred for 24 hours at room temperature with 400 ml of fuming sulphuric acid containing 3 percent of free sulphur trioxide. The residual oil, after separating it from the acid layer, washing, and drying, measured 1850 ml. Its refractive index was 1.4179.

To ascertain if the oil recovered from the acid treatment could now be further rectified, 1,800 ml was distilled at a pressure of 215 mm Hg through a 10-m column packed with steel jack chain. Under operating conditions believed to be most effective, the distillate was collected in 75-ml cuts. The whole fraction, with the exception of the first 10 percent which boiled a degree or two lower and whose refractive index averaged 0.003 higher, distilled over between 93.7 and 94.0° C. The refractive index of the successive cuts varied only between 1.4171 and 1.4176. As judged by the almost constant boiling point and refractive index of the distillation fractions, no significant separation had taken place. The middle portion of the distillate (80 percent of the total) when combined, boiled normally in a Cottrell apparatus at 136.1° C, had $n_{25}=1.4173$, $d_{15}=0.760$ g/ml, and congealed to a vitreous solid when cooled to −140° C.

The action of chlorosulphonic acid upon this material was observed to see if it would have a selective action on any constituent present, and thus effect a separation. A 10-ml sample of the oil was treated successively with 5 portions of the acid in 5-ml lots. Reaction with each portion was equally vigorous, the acid layer turning dark amber in color. The treatment was continued until half of the oil was destroyed. The remainder, when washed and distilled, had a refractive index of 1.4161, compared with 1.4173 for the original. Apparently, if the oil was a mixture of naphthene and paraffin hydrocarbons both classes were almost equally attacked.

When a sample of the distillate was cooled slowly, it would not crystallize. At −143° C it had become a clear, highly viscous, semi-solid mass. Obviously, then, the mixture of hydrocarbons could not be separated by crystallization from the oil itself. When, however, the oil diluted with twice its volume of propane was cooled and allowed to stand, a crystalline mass slowly developed, which at −140° C was exceedingly fine and pasty in texture. On whirling the mass in a centrifuge, crystals remained in the basket which were still pasty and contained a large amount of occluded propane. On removing the propane, the refractive indices of the fractions were as follows:

Crystal fraction	=1.4196
Mother liquor	=1.4166
Original oil	=1.4173

The higher refractive index of the crystal fraction was evidence that a naphthene hydrocarbon was concentrating in the solid phase.

When a mixture consisting of equal volumes of oil and propane was precooled to about −150° C and then added dropwise to a quantity of liquid methane equal in volume to the oil-propane mixture, crystals of good texture appeared which were separated from the liquid phase by centrifuging. After removing propane and methane, the different fractions had the following refractive indices:

Crystal fraction	=1.4219
Mother liquor	=1.4125
Original oil	=1.4173

It was apparent, from the large difference in refractive index between the crystal fraction and mother liquor, that a pronounced separation had taken place and that a systematic crystallization from a solution in liquid propane and methane by the procedure described by Leslie [8] would be an effective method for further separating the distillation fraction into its constituents. Using this procedure, there was obtained from the distillate a 100-ml fraction having the following properties: bp 760=136.7° C, fp=−78.5° C, $n^{25}{}_D$=1.4257, d_{25}=0.775 g/ml. The material was chiefly a naphthene, as indicated by its odor, density, and refractive index, but it was still impure as judged by the fact that it froze over a range of several degrees.

3. FURTHER FRACTIONATION OF THE DISTILLATE

Before attempting to isolate more of the detected naphthene, the distillation fractions shown in figure 2 were treated to free them more completely from aromatic hydrocarbons. The refractive indices of the fractions after this treatment are shown in graph III of figure 2. It may be observed in the figure that the indices for some of the fractions were thus lowered by about 0.005, corresponding to about 7 mole percent of aromatic hydrocarbons. For the fractions boiling near the boiling points of *p*- and *m*-xylene (about 97° C at 215) a greater lowering in refractive index was produced, amounting in the case of the 96 to 97° C cut to 0.008. This corresponds to a xylene content of about 10 mole percent. The analysis was borne out by a corresponding reduction in volume of the oil on treating with sulphuric acid.

[8] BS J. Research **10**, 609. (1933) RP552

In an effort to concentrate the naphthene further by distillation, the nine liters of acid-treated material, boiling between 93 and 95.5° C, was redistilled through 3-m columns packed with jewelers' locket chain.[9] The distillation was carried out under atmospheric pressure, in the presence of carbon dioxide gas, with a reflux ratio of about 20:1, and at a rate of 0.5 ml per minute. The distillate was collected in 50-ml cuts which were sorted and blended according to their boiling points and refractive indices. As a result the four blended fractions listed in table 1 were obtained.

TABLE 1.—*Properties of blended fractions obtained by distilling the acid-treated material boiling between 93 and 95.5°* C *at 215* mm *through columns packed with locket chain.*

Fraction	Volume	Boiling range (760)	n^{25}_D range
	ml	° C	
1	2850	135 to 136.0	1.4110 to 1.4135
2	1100	136.0 to 136.8	1.4135 to 1.4215
3	3850	136.8 to 137.0	1.4215 to 1.4230
4	1100	137.0 to 138	1.4224 to 1.4215

The first fraction was composed chiefly of isononanes. Work on its separation is now in progress. The fourth fraction consisted for the most part of a mixture of naphthenes. This was shown by the fact that when the material was fractionally crystallized the resulting fractions differed widely in freezing points (indicating a marked difference in composition) but possessed nearly the same relatively high refractive index. The second fraction of distillate was intermediate in composition between that of the first and third. The large volume of the third fraction (nearly 4 liters), its narrow boiling range, and its high refractive index, made it clear that here was a fraction highly concentrated in naphthenes.

Systematic crystallization of this 4 liters of material, boiling between 136.8 and 137° C, from a propane-methane solution yielded finally a series of fractions grouped according to table 2.

TABLE 2.—*Properties of some crystallization fractions*

Group	Volume	n^{25}_D	Boiling range	Freezing range
	ml		° C	° C
1	200	1.4271	136.65 to 136.7	−71 to −74
2	300	1.4255 to 1.4267	136.7 to 136.8	−75 to −80
3	200	1.4250 to 1.4255	136.8 to 136.9	−80 to −90

The mother liquor left from the crystallization had an average refractive index of 1.4223, boiled slightly higher than the listed fractions, and could not be further separated by crystallization. When it was redistilled, the successive fractions of distillate varied in boiling point from 136.8 to 137.3° C. The refractive index reached a maximum of n_{25}=1.4233 for the cut distilling at 137.1° C. The fractions

[9] S. T. Schicktanz, BS J.Research **11**, 89 (1933) RP579.

with boiling points below 137.0° C could be fractionated by crystallization; those boiling at and above 137.0° C could not. This fact indicates that the material boiling at this temperature was a mixture of naphthenes approaching their eutectic in composition. It was preserved for further separation at a future time.

4. CRYSTALLIZATION FROM DICHLORODIFLUOROMETHANE AND THE ISOLATION OF A NAPHTHENE BOILING AT 136.7° C

The moderately high melting point of the fractions, obtained by crystallization from solution in propane and methane, now made it possible to fractionally crystallize them further by a simpler method. Thus, preliminary experiments showed that when fractions having a refractive index of $n_{25} \gtreqless 1.423$ and boiling within a few tenths of a degree of 136.7° C (i. e., 136.5° to 136.8° C) were mixed with an equal or smaller volume of dichlorodifluoromethane and cooled, crystals of good texture would form which could be readily separated by centrifuging. Such mixtures froze initially at about −90° C for fractions having a refractive index of $n_{25} \gtreqless 1.4260$, at −135° C for a fraction with $n_{25}=1.4230$. A good crop of crystals was produced at a point 10° below the initial freezing point. The growth of crystals was slow, some time being required for "incubation" without stirring in order to get crystals of good texture instead of an amorphous mass. When crystallized in the manner described, the frozen material could then be fractionated further by allowing it to melt slowly in a centrifuge having a basket with an open top which permitted its contents to be stirred.

Systematic crystallization of the concentrated naphthene fractions from solution in dichlorodifluoromethane[10] coupled with fractional distillation finally produced a 200-ml sample of the naphthene which, after refluxing for 1 hour over sodium to remove all traces of solvent, was distilled and used for a study of its properties. It boiled at 136.7° C, melted between −66.3° and −65.7° C, had $n_{25}=1.4273$, and a density at 20° C of 0.7788 g/ml.

III. PROPERTIES OF THE ISOLATED NAPHTHENE

1. DEGREE OF PURITY

Before presenting an array of physical constants which will serve to identify a fraction of petroleum as a certain hydrocarbon it is first necessary to prove that the given fraction is substantially a single substance, not a mixture. As to purity of a sample of oil containing a known hydrocarbon one can be guided by comparing its physical constants with those of a sample of the pure material. In the case of an unidentified hydrocarbon this cannot be done. It then becomes necessary for evidence of purity to rely upon the vaporizing and freezing behavior of the substance.[11]

As a vaporizing test the distillation range of the 200 ml-sample, isolated by crystallizing from dichlorodifluoromethane, was determined by distilling it very carefully through a small, highly effective fractionating column and noting the boiling point of each successive 40 ml of distillate. The refractive index and melting range of the

[10] The dichlorodifluoromethane was furnished us through the courtesy of Kinetic Chemicals, Inc., Wilmington, Del. It boils at −30° C, remains limpid at low temperatures, and is nonflammable.
[11] Tests of this kind have been outlined by Washburn, Ind. Eng. Chem. 22 985 (1930).

fractions were also measured. The data for the first, middle, and residual fractions are recorded in table 3. The values are not absolute and are tabulated for comparative purposes only.

TABLE 3.—*Properties of fractions from the vaporizing test*

Fraction	Boiling point 760 mm	Melting point range		n_D^{25}
		Initial	Final	
	° C	° C	° C	
First	136.70	−66.4	−65.5	1.4272
Middle	136.70	−66.3	−65.6	1.4273
Residue	136.73	−66.8	−65.8	1.4273

From the data it is evident that each fraction of distillate had essentially the same values for the physical properties determined.

For the purpose of observing the behavior of the naphthene on cooling, the fractions from the distillation test were recombined, the whole

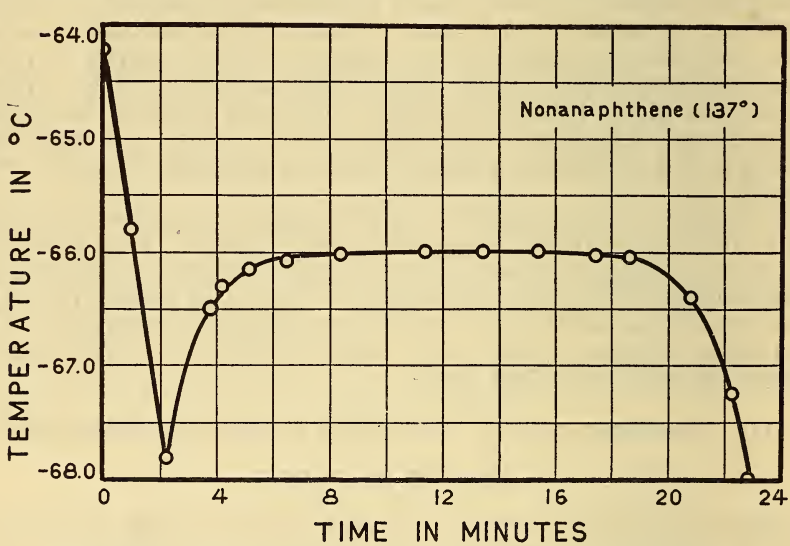

FIGURE 3.—*Time-temperature cooling curve of the nonanaphthene.*

sample frozen without solvent, and fractionated by melting. The last quarter to melt was used for the freezing test. In figure 3 is recorded the time-temperature cooling curve for the recrystallized sample. The prolonged halt in temperature, as shown by the region in the curve parallel to the time axis indicates that the sample froze almost entirely at a constant temperature.

The behavior of the material on distilling and freezing indicated that it was either a nearly pure substance or a mixture which was nearly constant-boiling and constant-freezing. Mixtures of the constant freezing type may be either eutectic mixtures or those forming solid solutions of components having the same or substantially the same freezing point. To see if an examination of the isolated material in the solid state would yield some information about its composition,

the growth and dissolution of its crystals were observed under the microscope.[12] On freezing, the hydrocarbon at first supercooled greatly and crystals which appeared were so fine-grained that interpretation of their nature was impossible. When, however, the crystals were allowed to melt almost completely and the material was slowly refrozen, the solid which persisted prevented a large amount of supercooling. The crystals which formed under these conditions were much larger, were composed of a single solid phase, and continued to grow until all was frozen. On melting, all crystals in a given region disappeared rapidly and apparently with the same velocity. Crystals were also produced by cooling a solution of the naphthene in an equal volume of ethyl ether. Here, too, only one solid phase appeared although the temperature was lowered from the initial freezing point (about −85° C) to about −135° C.[13] The formation of only one solid phase clearly showed that the fraction was no eutectic mixture.

Additional evidence concerning the composition of the material was obtained by determining its empirical formula. As a result of 3 determinations, the mean ratio, moles H_2O/moles CO_2, was found by the procedure given by Rossini[14] to be 0.9967 ± 0.0006 as compared with the calculated value, 1.1111 for a nonane C_9H_{20}, and 1.0000 for a nonanaphthene C_9H_{18}. Since all unsaturated and aromatic hydrocarbons, as well as solvent dichlorodifluoromethane, had been carefully removed from the sample, the ratio found by experiment indicates that any impurity present must be polycyclic rather than paraffinic in nature. The molecular weight, found by the lowering in freezing point of cyclohexane, was 126.3 ± 1.0 in good agreement with the calculated value of 126.15 for C_9H_{18}. From these values it is clear that the major constituent is a nonanaphthene or a mixture of nonanaphthenes.

When the results of the various tests are considered together, along with the fact that the material was isolated by fractional crystallization, there is a strong likelihood that the fraction of petroleum is chiefly a single substance. There is, however, a remote possibility that the fraction might be a mixture of isomers which on freezing forms a solid solution having substantially a constant freezing point.

2. PHYSICAL PROPERTIES

In table 4 are listed the physical constants of the sample whose freezing curve is shown in figure 3. It had the highest melting point of any fraction resulting from crystallization.

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[12] We are indebted to C. P. Saylor of this Bureau for the examination.

[13] In this connection it was found that on cooling an ether solution of a sample of the naphthene having a freezing range of 0.5° C and freezing initially 1° lower than the fraction described in this paper, a second solid phase did appear at a temperature where ether crystals could not possibly be coming out. This second solid phase may have contained another component, but it is equally possible, in this case, that it represented a second crystalline modification of the same component.

[14] BS J.Research 8, 121 (1932) RP405.

TABLE 4.—*The physical constants of a nonanaphthene from Oklahoma petroleum*

Normal boiling point	Freezing point	Specific gravity d_4^{20}	Refractive index n_D^{25}	Heat of fusion	cst in aniline
°C	°C			K cal/mol	°C
[a] 136.65 ±.05	[b] −65.80 ±.05	[c] 0.77883 ±.00002	[d] 1.42730 ±.00005 $dn/dt=-.00045$	[e] 2.79 ±.06	[f] 57.0 ±.5

[a] Determined with a Cottrell boiler.
[b] Temperature at which last crystals disappeared on melting.
[c] Determined by the Division of Weights and Measures of this Bureau.
[d] Determined with an Abbé refractometer (Valentine design).
[e] Determined by F. D. Rossini. See BS J.Research **11**, 553 (1933) RP607.
[f] Determined by R. T. Leslie. J.Research NBS **13**, 589 (1934) RP728.

The infrared absorption spectrum of the nonanaphthene was recorded by U. Liddel of the U. S. Bureau of Chemistry and Soils. The similarity of the absorptive index curve of the naphthene (figs. 4 and 5)

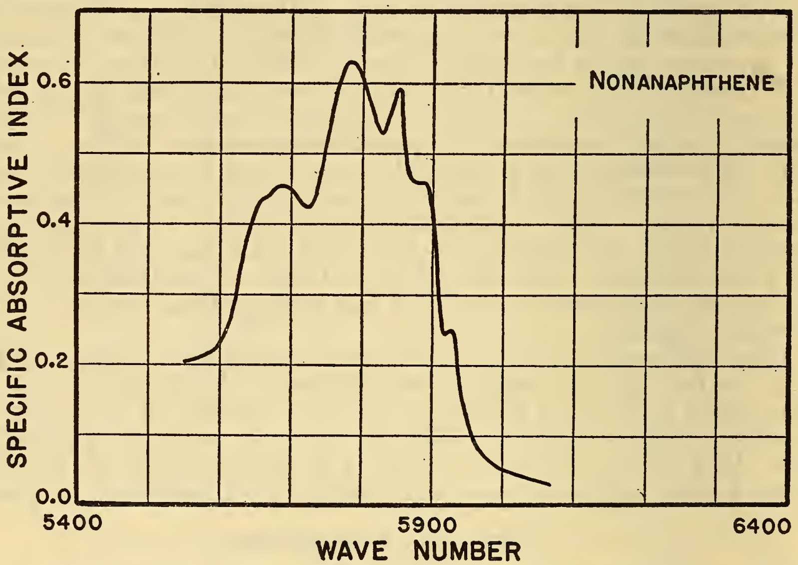

FIGURE 4.—*A portion of the infrared absorption spectrum of the nonanaphthene.*

to those of the hydrocarbon derivatives of cyclopentane [15] is evidence that the compound is a member of the cyclopentane series.

3. CHEMICAL PROPERTIES

Further indication that the compound is a cyclopentane derivative was revealed by its chemical behavior. Zelinsky and coworkers [16] have shown that palladium catalyzes the dehydrogenation of cyclohexane and its derivatives at 350 to 400° C, to form the corresponding aromatic hydrocarbons. The derivatives of cyclopentane, on the contrary, were found to be stable under these conditions. When the vapors of our material were passed repeatedly over palladium asbestos at 350 to 380° C, only a slight evolution of hydrogen occurred. The refractive index of the recovered oil was 1.4305 as compared

[15] Liddel and Kasper, BS J.Research **11**, 599, figure 5 (1933) RP610.
[16] Ber. Deut. Chem. Ges. **45**, 3678 (1912); **56** [**B**], 1718 (1923).

with 1.4273 for the original. This indicated that very little aromatic hydrocarbon had been produced. Contrary to this behavior, 1,3,-5-trimethylcyclohexane, when treated in a similar manner, was readily dehydrogenated into mesitylene, the corresponding aromatic hydrocarbon.

The result of the attempted dehydrogenation of our nonanaphthene strongly signifies that it is not a cyclohexane derivative. This evidence alone is not conclusive, for it is known that the dehydrogenation test fails to distinguish between a cyclopentane derivative and cyclohexane derivatives containing a *gem* dialkyl group.[17] The latter compounds, containing a completely substituted carbon atom in the ring, cannot be regarded as derivatives of "hexahydrobenzene" because they cannot be dehydrogenated to aromatic hydrocarbons. Zelinsky found this to be the case for 1,1-dimethylcyclohexane.

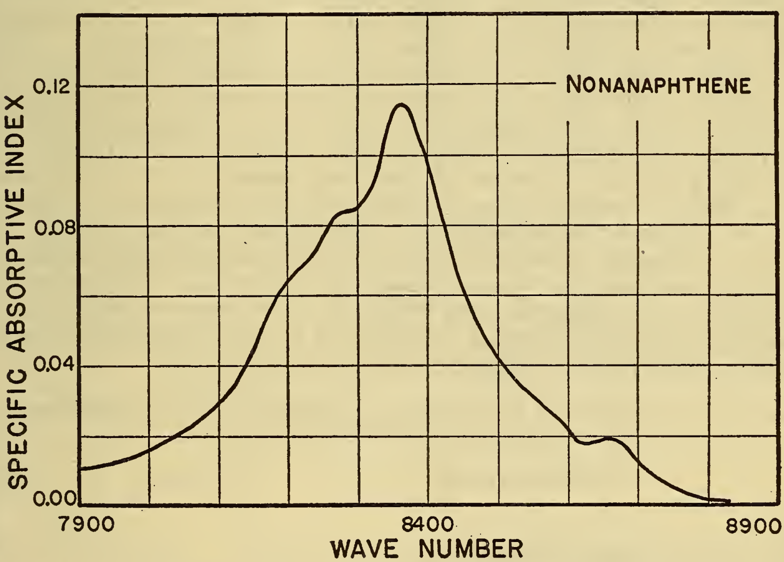

Figure 5.—*A portion of the infrared absorption spectrum of the nonanaphthene.*

That our compound is probably no cyclohexane derivative of this type is shown by the fact that all the known nonanaphthenes which are cyclohexanes having a *gem* dialkyl linkage boil at temperatures well above 137° C.

When treated with the nitrating mixture referred to earlier in this paper, the isolated nonanaphthene was oxidized without forming a nitro product. On the contrary, 1,3,5-trimethylcyclohexane, when treated with the same reagent, formed an appreciable amount of a nitro compound. This experiment is also evidence that the petroleum product is not a derivative of cyclohexane.

IV. POSSIBLE IDENTITY OF THE ISOLATED NONANAPHTHENE

Markownikoff and Ogloblin detected the presence of a nonanaphthene in a Baku petroleum distillate which boiled at 135 to 136° C.[18]

[17] Ber. Deut. Chem. Ges. **56** [**B**], 1716 (1923).
[18] Ber. Deut. Chem. Ges. **16** [**B**], 1873 (1883).

It too would form no nitro-product. The density of the distillate (0.7652 at 20° C) was definitely lower than that of our material, indicating that it was a mixture of naphthene and isononane. The boiling range of their fraction, however, was the same as that for the distillate in which the nonanaphthene of this investigation was first discovered. Zelinsky likewise was able to detect the presence of a nonanaphthene, which could not be dehydrogenated, in the distillation fraction of Baku petroleum boiling between 136 and 137.5° C.[19] Combustion analysis indicated, however, that it also was a mixture of naphthene and isononane.

It is possible that in each case the same nonanaphthene has been encountered. Assured that our compound is a derivative of cyclopentane, one is still confronted with which of the large number of possible cyclopentane derivatives containing nine carbon atoms it might be. The compound must be one of the isomers of the following: tetramethylcyclopentane, methylpropylcyclopentane, dimethylethylcyclopentane, diethylcyclopentane, and butylcyclopentane. When one reflects that most of these hydrocarbons exhibit space, as well as structural isomerism, the number of possibilities becomes amazing. A few of these nonanaphthenes have been synthesized and their properties determined.[20] Of the known members of the family, very few boil near 137° C; most of them boil above 140° C. By boiling point alone a number of possibilities are thus eliminated. Some of the dimethylethylcyclopentanes, however, are known to boil near 137° C. Possibly other derivatives of cyclopentane boil at this temperature also but their properties are not recorded. The probability that the nonanaphthene from Oklahoma petroleum is related to the dimethylethylcyclopentanes is indicated by the approximate agreement in their physical properties as shown in table 5.

TABLE 5.—*Comparison of the properties of nonanaphthene from petroleum with those for 2 dimethylethylcyclopentanes*

Nonanaphthene C_9H_{18}	Boiling point	d_4^{20}	n_D^{25}
	°C		
From Oklahoma petroleum. White and Rose	136.65	0.7788	1.4274
1, 4-dimethyl-2-ethylcyclopentane. Zelinsky and Pappe, J. Russ. Phys. Chem. Soc. **37**, 627(1905)	135.5 to 137	.7700	1.4213
1, 3-dimethyl-2-ethylcyclopentane. Zelinsky and Glinka, J. Russ. Phys. Chem. Soc. **39**, 1170(1907)	135 to 137	.7703	----------

V. CONCLUSION

The complete identification of the nonanaphthene must await further investigation. Even if its structural formula could be established, the question as to which stereoisomer (cis or trans) it was, would still require answering. The determination of the amount of this hydrocarbon in Oklahoma petroleum must also be postponed until a study of the naphthene fraction boiling immediately above it is completed. From the four liters of mixture which distilled over between 136.8 and 137° C it is safe to say that the crude oil contains not more than 0.1 percent of the nonanaphthene boiling at 136.65° C.

We wish at this time to acknowledge gratefully the advice of the late Dr. E. W. Washburn, who, before his death, directed this research.

WASHINGTON, August 16, 1934.

[19] Ber. Deut. Chem. Ges. **56** [**B**], 1718 (1923).
[20] Beilstein's Handbuch, 4th ed., Ergänzungswerk, **V**, 18–19.